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brighter as to give the character in question. What strikes one most, however, is the varying relative brightness of the continuous and linear spectra; sometimes the lines are scarcely seen, and sometimes very little else is seen. This may be nothing more than an illusion; but in the absence of any certainty that it is so, the impression left on the mind is worth recording.

The difficulty of discriminating between the many less prominent lines is immensely increased by the momentary character of the phenomenon. Before the mind has selected an individual, the feeble impression on the retina has vanished; and before another flash succeeds, the memory of the half-formed choice has vanished with it, and there is nothing on which to found a selection. Otherwise it would be easy enough to measure many more lines.

III. "Products of the Destructive Distillation of the Sulphobenzolates.  
—No. II." By JOHN STENHOUSE, LL.D., F.R.S., &c. Received September 8, 1868.

In a paper published by me in the Proceedings of the Royal Society, 1865, I described the manner of preparing sulphobenzolate of sodium and the products of its destructive distillation in a copper retort. These were chiefly sulphide of phenyl and a crystalline substance, of which too small a quantity was obtained to enable me properly to examine it.

As I wished to procure these products in larger quantities, instead of employing small copper retorts, which were rapidly destroyed, I conducted the operation in tolerably large cast-iron ones heated in a gas-furnace, and found that they were not sensibly corroded even after a great number of distillations. The quantity of sodium-salt decomposed in each distillation was about 200 grammes.

The oily products obtained by this process, after separation from the supernatant watery layer, were introduced into a copper retort having a bent glass tube luted into the neck and redistilled, the retort being heated to redness towards the close of the operation. In this way a considerable amount of impurity was removed. The bright yellow-coloured oil was then rectified in a glass retort. It began to boil at 80° C., and rose rapidly to 165° C., between which and 180° C. about one-fourth of the liquid came over. The temperature then again rose rapidly to 290° C., and from 290° to 300° a large quantity of nearly pure sulphide of phenyl distilled. The small quantity of dark-coloured residue in the retort was poured into a beaker, where it became semisolid on cooling from the deposition of the crystalline substance I have before mentioned\*.

*Phenyl-Mercaptan.*

The portion boiling between 165° C. and 180° C., on being repeatedly rec-

\* Proc. Roy. Soc. vol. xiv. p. 353.

tified, gave a liquid boiling constantly at  $172^{\circ}5$ . This was subjected to analysis with the following results :—

I. '5345 grm. oil gave 1.280 grm. carbonic anhydride and '265 grm. water.

	Theory.	I.
$C_6 = 72$	65.45	65.33
$H_6 = 6$	5.45	5.51
$S = 32$	29.10	
110	100.00	

The numbers obtained correspond very closely with the formula  $C_6 H_5 \left\{ \frac{H}{S} \right\} S$ , *phenyl-mercaptan*. When pure it is colourless, having an aromatic but somewhat alliaceous odour, although not at all offensive. It has a high refractive index, and boils at  $172^{\circ}5$  C. Insoluble in water, but readily miscible with alcohol, ether, and benzol. It is readily oxidized, yielding bisulphide of phenyl. This takes place even when exposed to the air in imperfectly closed vessels.

Vogt\* has described an oil which he obtained by the action of zinc and dilute sulphuric acid on sulphobenzolic chloride,  $C_6 H_5 Cl S O_2$ , and calls *benzyl-mercaptan*,  $C_6 H_6 S$ . He says it boils at "about  $165^{\circ}$  C., and has an extremely offensive odour."

Otto†, by the action of nascent hydrogen on sulphophenylenethylene,  $C_6 H_4 S O_2 \left\{ C_2 H_4 \right\}$ , obtained phenyl-mercaptan, which he showed to be identical with Vogt's benzyl-mercaptan, but the boiling-point is "between  $170^{\circ}$  C. and  $173^{\circ}$  C."

From the description given by Vogt and Otto, it is evident that the phenyl-mercaptan obtained by the destructive distillation of sulphobenzolate of sodium in an iron retort is identical with theirs, and that the offensive odour ascribed to it by Vogt is due to some slight impurity, probably arising from the phosphoric chloride employed in the preparation of the sulphobenzolic chloride.

*Phenyl-mercaptide of lead*.—On adding acetate of lead to an alcoholic solution of the mercaptan, a bright yellow crystalline precipitate was formed. This when heated fused, and at a higher temperature was decomposed.

*Phenyl-mercaptide of copper* was prepared in a similar manner, substituting acetate of copper for acetate of lead. On exposure to the air in a moist state it became oxidized, forming cupric oxide and bisulphide of phenyl,  $C_6 H_5 S$ , which may be extracted and crystallized from boiling spirit.

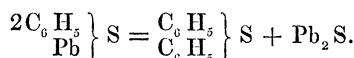
The compounds with mercury, chloride of mercury, and silver are identical with those described by Vogt.

\* Ann. der Chem. und Pharm. vol. cxix. p. 144.

† Ibid. vol. cxlii. p. 211.

*Decomposition of Phenyl-mercaptide of Lead.*

When dry phenyl-mercaptide of lead is heated to a temperature superior to 280° C. it is decomposed, an oil distils over, and plumbic sulphide is left in the retort. This oil boils constantly at 292°.5 C., and corresponds in all its properties with *phenylic sulphide*. By oxidation it yielded a substance crystallizing in oblique prisms, and which was proved to be sulphonbenzolene. The action of heat on the lead mercaptide is therefore as follows :—



This decomposition is especially interesting, as it proves the body obtained by the destructive distillation of the sulphonbenzolates to be the true phenylic sulphide.

*Bisulphide of Phenyl.*

When the pure mercaptan was mixed with about an equal bulk of concentrated sulphuric acid, the latter acquired a dirty purple colour, and after the lapse of some time, with occasional agitation, became hot and gave off sulphurous anhydride. When cold the upper layer solidified to a mass of crystals, which, on being separated from the acid, washed with water, and crystallized several times from spirit, gave a white crystalline substance. It was dried *in vacuo* and analyzed.

I. ·308 grm. substance gave ·745 grm. carbonic anhydride and ·133 grm. water.

	Theory.	I.
C <sub>6</sub> = 72	.... 66.05	.... 65.98
H <sub>5</sub> = 5	.... 4.59	.... 4.80
S = 32	.... 29.36	
	109	100.00

The analysis corresponds to the formula C<sub>6</sub>H<sub>5</sub>S, *bisulphide of phenyl*. It is insoluble in water, soluble in alcohol, very soluble in ether, benzol, and bisulphide of carbon, melts at 61° C. (Vogt\* gives 60° C. as the melting-point of his bisulphide of benzyl). It is again reduced to the mercaptan by zinc and dilute sulphuric acid, or better, by digestion with hydriodic acid and amorphous phosphorus.

As but traces of phenyl-mercaptan were obtained on decomposing the sulphonbenzolates of sodium in a copper retort, while a considerable portion of the distillate consisted of the mercaptan when an iron one was used, I was induced to make some experiments in order to see whether it was the copper which caused this difference. This I ascertained to be the case by distilling sulphonbenzolates of sodium mixed with copper cuttings in an iron retort, when the proportion of the mercaptan to the sulphide was comparatively small, and the surface of the copper was converted into cupric sulphide. Granulated zinc produced a similar result.

\* Ann. der Chem. und Pharm. vol. cxix. p. 149.

*Phenylene Sulphide.*

The dark-coloured residue in the retort which did not come over at 300° C. was distilled from a copper retort having a bent glass tube luted into it. The orange-coloured distillate, on standing a few days, deposited a considerable quantity of large transparent plates. These were drained as much as possible, and freed from adhering oil by pressure between paper. The partly purified crystals were extracted with hot spirit to remove the bisulphide of phenyl and other impurities, and then crystallized from benzol or bisulphide of carbon. A crystallization from spirit rendered them quite pure.

I. ·243 grm. gave ·592 carbonic anhydride and ·086 grm. water.

II. ·221 grm. gave ·539 carbonic anhydride and ·076 grm. water.

III. ·301 grm. gave ·652 baric sulphate.

	Theory.	I.	II.	III.	Mean.
C <sub>6</sub>	= 72 ..	66·67	66·45	66·53	.... 66·49
H <sub>4</sub>	= 4 ..	3·70	3·93	3·82	.... 3·87
S	= 32 ..	29·63	....	....	29·71 29·71
	108	100·00			

The analyses of this substance lead to the formula C<sub>6</sub>H<sub>4</sub>S, *sulphide of phenylene*. It crystallized in long lustrous prisms, which are quite transparent and colourless. Is insoluble in water, slightly soluble in cold alcohol (about 400 parts), but more so in hot. It is far more soluble in benzol and bisulphide of carbon, from the latter of which it may be obtained in fine crystals, sometimes half an inch or more in length. It melts at 159° C. and solidifies at 153° C. It dissolves in concentrated sulphuric acid, forming a solution of a magnificent purple colour, and which when largely diluted with the concentrated acid appears purplish red. On the addition of water the colour disappears, and a crystalline precipitate is produced, apparently the unaltered phenylene sulphide. With concentrated nitric acid a reaction takes place, red fumes are evolved, and a crystalline substance produced, probably a nitro-substitution compound. This I have at present under investigation.

*Sulphobromide of Phenylene.*

When crystals of the phenylene sulphide are exposed to bromine-vapour they combine with it and turn black, forming sulphobromide of phenylene. The best method, however, to obtain this pure, is to add perfectly dry bromine in slight excess to a cold saturated solution of sulphide of phenylene in dry bisulphide of carbon, when the compound is precipitated in the form of minute black prisms. These are immediately collected, washed with cold dry carbonic disulphide, pressed, and the bisulphide of carbon removed by placing them under the receiver of an air-pump, rapidly exhausting the air, and allowing it to reenter several times. It is then

66 *On the Destructive Distillation of the Sulphobenzolates.* [Recess,

weighed and treated with excess of pure solution of sulphurous acid, to convert the combined bromine into hydrobromic acid. This is determined as bromide of silver. By this method the following result was obtained :—

•821 grm. substance gave 1•154 grm. argentic bromide. This gives 59•81 per cent. combined bromine. The formula  $C_6H_4SBr_2$  requires 59•70 per cent. bromine. This substance is therefore analogous to the corresponding ethylene compound discovered by Carus\*.

The sulphobromide crystallizes in black prisms, which slowly give off bromine on exposure to dry air, and are rapidly decomposed by moisture with evolution of hydrobromic acid. They are tolerably soluble in carbonic disulphide and tetrachloride.

*Phenyl-hyposulphurous Acid.*

Amongst the reactions which phenylic sulphide gave with various reagents†, that with sulphuric acid was particularly interesting. On treating pure sulphide of phenyl with an equal bulk of concentrated sulphuric acid, the oil changed first to a fine red colour, and as the heat increased it became purple, and ultimately dissolved, giving off traces of sulphurous acid. The compound thus produced, when cold, was semifluid, and gradually absorbed moisture from the air, becoming a semisolid crystalline paste. This was dissolved in a large quantity of boiling water, neutralized with *pure* baric carbonate, filtered from the insoluble sulphate, and the solution of phenyl-hyposulphite of barium evaporated until a pellicle formed on the surface, and then allowed to cool.

The crusts which come out consist of microscopic crystals. These, after one or two recrystallizations from boiling water, were dried at 100° and submitted to analysis.

•419 grm. substance gave •175 grm. baric sulphate.

•334 grm. substance gave •141 grm. baric sulphate.

•320 grm. substance gave •312 grm. carbonic anhydride and •075 grm. water.

	Theory.	I.	II.	III.
$C_6$ = 72	.. 26•13	..	..	26•61
$H_7$ = 7	.. 2•54	..	..	2•61
$Ba$ = 68•5	.. 24•85	24•56	24•82	
$S_2$ = 64	.. 23•24			
$O_4$ = 64	.. 23•24			
	275•5	100•00		

These analyses agree tolerably well with the formula  $C_6H_5BaS_2O_3 \cdot H_2O$ , which I propose to call baric phenyl-hyposulphite. I have prepared the copper salt, which likewise forms crystalline crusts ; but neither the calcium nor sodium salt crystallizes as well as the barium.

\* Ann. der Chem. und Pharm. vol. exxiv. p. 113.

† Proc. Roy. Soc. vol. xiv. p. 354.

It is not improbable that ethylic and methylic sulphides, &c., when treated with concentrated sulphuric acid, would form corresponding compounds.

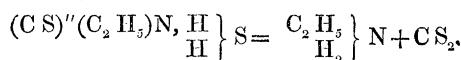
I cannot conclude this paper without acknowledging the very efficient aid I have received from my assistant, Mr. Charles E. Groves, in the preceding investigation.

IV. "Compounds Isomeric with the Sulphocyanic Ethers.—II. Homologues and Analogues of Ethylic Mustard-oil." By A. W. HORNAMMANN, Ph.D., M.D., LL.D. Received September 11, 1868.

In a former Note submitted to the Royal Society some months ago\*, I have sketched a series of compounds isomeric with the well-known sulphocyanic ethers; today I shall endeavour to delineate more in detail the bodies the existence of which I then pointed out.

In order to prepare these substances, which, from their analogy with the essential oil of mustard-seed, I have designated by the name of *mustard-oils*, the monamines were in the first place treated with bisulphide of carbon; the alcohol-sulphocarbonates of the monamines thus formed were then submitted to the action of heat and converted, by the loss of 1 molecule of sulphuretted hydrogen, into sulphuretted ureas, which were finally deprived of 1 molecule of monamine by means of anhydrous phosphoric acid. Circuitous as this process may appear, it has the merit of being a general one, furnishing, in fact, the mustard-oils both of the fatty and aromatic series. When working with fatty substances, however, the method may be very considerably curtailed. Let it be *ethylic mustard-oil* that is to be prepared.

Even on the threshhold of my inquiry I had hoped to see ethyl-sulphocarbamic acid split up into sulphuretted hydrogen and ethylic mustard-oil; experiment, however, proved that the metamorphosis assumes another form, the acid yielding as products of decomposition its two components, ethylamine and bisulphide of carbon.



But a transformation which the free acid refuses, the metallic ethyl-sulphocarbamates undergo without difficulty, more especially in the presence of an excess of the metallic solution, a metallic sulphide being formed.



On adding, for instance, nitrate of silver to a solution of ethyl-sulphocarbamate of ethylamine, such as is produced by the action of bisulphide of carbon upon ethylamine, a white precipitate of ethyl-sulphocarbamate of silver is formed, nitrate of ethylamine passing into solution. After some time,

\* Proceedings, vol. xvi. p. 254.